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The Chemical Equilibrium Problem: an Application of SUMT

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The Chemical Equilibrium Problem:

an Application of SUMT

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FOREWORD

This paper deals with the determination of the equilibrium concentration of multiphase-reacting chemical systems. This type of problem is of paramount interest in many contemporary technologies and in recent years has attracted the attention of the mathematical community. The reason this particular problem is of interest is that it can be formulated as a mathematical nonlinear programming problem. In keeping with RAC's research interest in nonlinear programming, in particular the sequential unconstrained minimization technique (SUMT), it is felt that it is of great importance to illustrate the power of SUMT in obtaining the solution of moderate-sized problems. Inasmuch as many groups are concerned with developing special algorithms for solving the chemical equilibrium problem, the application of the general SUMT to this problem is presented here.

It is felt that it is necessary to document the practical application of SUMT as well as the theoretical developments, and this problem is of a size that again demonstrates the power of the technique.

Nicholas M. Smith
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The Chemical Equilibrium Problem: an Application of SUMT

ABSTRACT

The equilibrium composition of homogeneous chemical reactions is a very important problem in studies of complex chemical systems that arise in the study of certain physiological systems, rocket-propulsion systems, reentry problems, etc. The aim of this report is to show that the sequential unconstrained minimization technique (SUMT) as exploited by Fiacco and McCormick is capable of solving this problem and indeed offers distinct advantages over the heretofore best available computational techniques such as those presented by White et al[1] and DeHaven and Deland.[2] The power of this method for solving moderate-sized problems is illustrated by the choice of a 45-variable problem with 16 linear equality constraints.

1. INTRODUCTION

The problem of determining the equilibrium composition of homogeneous chemical reactions can be shown, in a great number of cases, to be equivalent to finding that composition vector that results in minimizing the Gibbs-Helmholtz free energy of a chemical system and simultaneously satisfying the requirements of mass balance. This observation replaces a chemical problem with a mathematical problem: find a vector that minimizes a certain function subject to the satisfaction of a system of linear equations that are the formal expression of the mass-balance law.

The intent of this report is to show that SUMT as exploited by Fiacco and McCormick[3-6] is a method that offers distinct advantages over preexisting methods that were developed for this particular problem.[1,7] Until recently,[8] all these methods depended for their solution on the availability of positive estimates of the solution. Advantage has also been taken of the special structure of this problem to greatly enhance the rate of convergence of the minimization technique utilized in SUMT.

2. THE SUMT ALGORITHM

A brief discussion of SUMT for nonlinear programming is presented in this section. No pretense is made of being very detailed, and the reader is referred to the basic works on the subject as given in Fiacco and McCormick.[3-6] Consider now the solution of the general nonlinear programming problem:

Minimize

$$f(x)$$

subject to (A)

$$h_j(x) = 0, \quad j = 1,\ldots,p$$

$$g_i(x) \geq 0, \quad i = 1,\ldots,m,$$

where $x \in E^n$, i.e.,

$$x = \begin{bmatrix} x_1 \\ x_2 \\ \cdot \\ \cdot \\ \cdot \\ x_n \end{bmatrix}.$$

The SUMT algorithm for the solution of this problem is as follows:

(a) Form the function

$$P(x, r_k) = f(x) + r_k \sum_i 1/g_i(x) + r_k^{-\frac{1}{2}} \sum_j h_j^2(x).$$

(b) Find the unconstrained minimum of the P function in the region $\{x \mid g_i(x) > 0, i = 1, \ldots, m\}$ for each fixed r_k, where $\{r_k\}$ is a decreasing sequence of positive numbers such that $\lim_k r_k = 0$.

It will follow that, under certain reasonable restrictions, the sequence of values of the P function $\{P(x;r_k)\}$, respectively minimized by $\{x(r_k)\}$ over the strictly monotone sequence $\{r_k\}$, converges to the optimum value of f.

At this point it would not be amiss to point out that the method SUMT uses to find the unconstrained minimum of $P(x;r)$ is a modified Newton's method. That is to say, starting with an initial estimate, for fixed r, one determines the next move as follows:

$$x^{n+1} = x^n - \theta[\nabla^2 P(x^n;r)]^{-1} \nabla P(x^n;r).$$

The parameter θ is a scale parameter whose determination may vary lending rise to different types of algorithms for minimization. This point is not discussed in this paper. The essential thing to observe here is the difficulty that could arise in the determination of the inverse of the matrix $\nabla^2 P(x;r)$. Note also that if the function f is convex and the functions g_i are concave and if the h_i's are linear then the resultant P function is convex, and hence when the feasible region has a nonempty interior the problem before us is to find the unconstrained minimum of a convex function.

If it should turn out that the matrix $\nabla^2 P(x;r)$ can be put in the form $A + u\sigma v^T$, where A is an $n \times n$ matrix, u is an $n \times p$ matrix, σ is a $p \times p$ matrix, and v^T is a $p \times n$ matrix, then the following formula may be used for computing $[A + u\sigma v^T]^{-1}$.

$$[A + u\sigma v^T]^{-1} = A^{-1} - A^{-1}u[\sigma^{-1} + v^T A^{-1} u]^{-1} v^T A^{-1}. \qquad (1)$$

If the matrices A and σ are easily invertible then it is obvious that this method ("rank annihilation") is extremely powerful.

It is also the intent of this paper to show that by using this method of matrix inversion the SUMT can be brought to bear to solve some medium-sized mathematical programming problems, collectively called the "chemical equilibrium problem," that arise in various scientific and technological areas. The main advantages of this method of matrix inversion when applicable is that it greatly enhances the rate of convergence of the SUMT algorithm.

3. THE CHEMICAL EQUILIBRIUM PROBLEM

The chemical equilibrium problem is the determination of the composition of the chemical species that minimizes the (Gibbs) free energy of a chemical system and must also satisfy the mass conservation law in the form of the mass balance equations. Mathematically speaking, the problem is as follows:

Minimize

$$F(x),$$

where

$$F(x) = \sum_{k=1}^{p} \left\{ \sum_{j=1}^{n_k} x_{jk} \left[c_{jk} + \ell n \left(x_{jk} / \sum_{i=1}^{n_k} x_{ik} \right) \right] \right\}$$

subject to

$$Hx = b \text{ and } x \geq 0$$

where

$$b = (b_1, \ldots, b_q)^T, \qquad x = (x_{11}, x_{21}, \ldots, x_{n_p,p})^T.$$

In this description a chemical system (mixture) is considered to be a system composed of a number of different molecules of various species existing in p various phases, e.g., physical compartments, conceptual compartments, or a gas, liquid, or solid. It is to be emphasized that the same molecule in a different phase is to be considered a different molecular species. Assume that all the different species occurring in the system are composed of some finite set of basic ingredients, which may be molecules, atoms (both charged and uncharged), and possibly pure charge. The only requirement is that all the reaction products be combinations of these basic ingredients, or this basic

"alphabet." The determination of what is a possible reaction product is of course left in the hands of the chemist who might be applying this method. Presumably he can determine a priori what the possible nontrace amounts of the reaction products will be. For instance, if there are b_j atomic weights of basic unit j originally in the system and M different units in the basic alphabet, then at the end of reaction, i.e., at equilibrium, the total amount of basic unit j will be b_j. The linear system $Hx = b$ just represents the fact that mass is conserved in the system. The matrix H is a matrix whose (i,j)th entry gives the number of basic "letter" j in molecular species i. In the mathematical formulation it is assumed that there are q elements (letters) in the basic alphabet so that the matrix H is $q \times N$ and of course the "state" vector ("composition" vector) is $1 \times N$, where there are n_p chemical species in the pth phase and $N = n_1 + n_2 \ldots + n_p$. The constants c_{jk} occurring in the expression for $F(x)$ are called "free-energy constants" and are obtainable from tables. The (i,j)th component of the state vector, namely, x_{ij}, represents the number of moles of species j in compartment (phase) i. For more detail on the physical problem, applications, and extensions see Refs 1, 2, and 7 to 12.

Now observe the special form of the matrix of second partial derivatives of the function $F(x)$:

$$\nabla^2 F(x) = \operatorname{diag}(1/x_{\alpha\beta}) + \sum_{i=1}^{p} I_i \left(-1/\sum_{\ell=1}^{n_i} x_{\ell i}\right) I_i^T,$$

where α is $1,2,\ldots,n_\beta$, β is $1,\ldots,p$, and I_i is an $N \times 1$ vector with 1's in the positions associated with $(x_{1i}, x_{2i}, \ldots, x_{n_i i})$ as it appears in the vector x and zeros elsewhere. The matrix of second partial derivatives of P is thus given by

$$\nabla^2 P(x;r) = \operatorname{diag}(1/x_{\alpha\beta} + 2r/x_{\alpha\beta}^3) + \sum_{i=1}^{q} h_i \left[2r/(h_i^T x - b_i)^3\right] h_i^T + \sum_{\ell=1}^{p} I_\ell \left(-1/\sum_{i=1}^{n_\ell} x_{i\ell}\right) I_\ell^T. \tag{2}$$

where h_i^T is the ith row of H, and of course $\alpha = 1,2,\ldots,n_\beta; \beta = 1,\ldots,p$. If $A = \operatorname{diag}(1/x_{\alpha\beta} + 2r/x_{\alpha\beta}^3)$, $u_i = h_i$, $v_\rho = I_\ell$, $\sigma_1^i = 2r/(h_i^T x - b_i)^3$, and $\sigma_2^\ell = \left(-1/\sum_{i=1}^{n_\ell} x_{i\ell}\right)$, Eq 2 can be put in the form

$$\nabla^2 P(x;r) = A + \sum_{i=1}^{q} u_i \sigma_1^i u_i^T + \sum_{\ell=1}^{p} v_\rho \sigma_2^\ell v_\ell^T. \tag{3}$$

Since A is a diagonal matrix and $\{\sigma_1^i\}$, $\{\sigma_2^\ell\}$ are scalars, it may be seen immediately that Eq 3 is of the desired form, and to invert $\nabla^2 P(x;r)$, merely apply Eq 1 $p + q$ times. This is not prohibitive because of the simple form of the matrices involved.

The method used in DeHaven and Deland[2] as presented by White et al and Clasen[1,7] is mentioned briefly. This method is in essence to seek an approximate positive solution $y = (y_{11}, y_{21}, \ldots, y_{n_p p})^T$ to the system $Hx = b$. Then the free-energy function F is expanded in a Taylor series about y. This can be done because y is positive. All but the second-order terms are discarded, leaving a quadratic approximation $Q(x)$ to $F(x)$. This quadratic $Q(x)$ is then minimized using a simple gradient descent method to give a "better" approximation to the minimum of F. The cycle is then repeated on Q using this new value for the approximate minimum. It is to be noted that the better the initial estimate the more effective the algorithm, but convergence cannot be guaranteed. However, by applying SUMT with the knowledge that the problem is a convex problem, convergence is guaranteed.

4. EXAMPLE

As a numerical example of moderate size consider the Lung Level Respiration Model presented by DeHaven and Deland.[2] The data are repeated in Fig. 1 with the exception that, as indicated in Table 1, an initial vector $x = (0, \ldots, 0)$ is used. In this problem, $p = 7$, $q = 16$, and $N = 45$. Note that in DeHaven and Deland 11 of the 56 variables are kept at zero and hence do not enter into the computations.

The solution, shown in Table 1, was obtained on an IBM 7044, 32-K, IBSYS version 9.9 computer in 3.58 min. This is to be compared with the solution given by DeHaven and Deland, where the initial vector is somewhat "close" to the optimal vector and where the method presented in White et al[1] was utilized. No computing times were given by DeHaven and Deland, and hence a time comparison of the methods cannot be made. It is to be noted, also, that there are differences in the solution vectors for the small components. The reason for this will be investigated in the future. Note also that

TABLE 1

Comparison of DeHaven and Deland Solution with SUMT Solution

DeHaven and Deland[2]		SUMT	
Initial point	Solution	Initial point	Solution
6.0000000E-01	6.4400600E-01	0.00E-00	6.4399658E-01
2.0000000E-01	2.5895000E-01	0.00E-00	2.5896960E-01
3.0000000E-01	3.7048000E-00	0.00E-00	3.7048090E-00
3.0000000E-01	2.9966000E-01	0.00E-00	2.9966666E-01
6.7500000E-05	6.7477199E-05	0.00E-00	5.6165829E-05
7.0000000E-04	6.9966500E-04	0.00E-00	6.8800160E-04
2.1700000E-04	2.7131800E-04	0.00E-00	2.0617855E-04
2.1000000E-08	5.3669300E-07	0.00E-00	1.1005665E-06
3.0500000E-07	8.9100400E-07	0.00E-00	2.4329989E-06
5.8500600E-02	5.7593800E-02	0.00E-00	5.7145151E-02
8.0500000E-02	7.9857600E-02	0.00E-00	7.9380462E-02
4.0000000E-03	3.3371600E-03	0.00E-00	3.2310024E-03
2.8950000E-01	2.8821100E-01	0.00E-00	2.8387379E-01
1.3500000E-02	1.4007900E-02	0.00E-00	1.3878336E-02
9.9200000E-07	1.4247100E-06	0.00E-00	3.2831591E-06
1.8500000E-05	1.9695800E-05	0.00E-00	1.7377889E-05
8.8000000E-03	1.1553100E-02	0.00E-00	1.1551705E-02
6.8700000E-05	6.8360400E-05	0.00E-00	5.9559742E-05
4.3400000E-04	4.3427300E-04	0.00E-00	4.4194828E-04
2.2200000E-04	2.2238900E-04	0.00E-00	2.2045284E-04
2.0900000E-08	5.5183199E-07	0.00E-00	1.0947029E-06
1.1800000E-07	6.8250600E-07	0.00E-00	1.8516727E-06
2.2900000E-02	2.2458600E-02	0.00E-00	2.2906192E-02
4.6000000E-03	8.2744299E-03	0.00E-00	8.7509019E-03
5.0000000E-02	4.4955000E-02	0.00E-00	4.5060355E-02
1.7950000E-01	1.7888700E-01	0.00E-00	1.8322359E-01
6.1300000E-03	6.2844200E-03	0.00E-00	6.3957550E-03
6.1700000E-07	1.0429000E-06	0.00E-00	2.8552963E-06
5.2800000E-06	5.6044400E-06	0.00E-00	7.8058135E-06
1.8700000E-02	2.1130000E-02	0.00E-00	2.1129053E-02
1.2000000E-08	7.9731300E-06	0.00E-00	7.4288879E-06
1.0000000E-07	3.3106700E-05	0.00E-00	3.0172473E-05
5.8000000E-06	5.5210300E-05	0.00E-00	5.0560606E-05
6.4000000E-05	5.5219900E-05	0.00E-00	4.8710919E-05
2.2300000E-03	2.1269900E-03	0.00E-00	2.1419671E-03
4.7000000E-05	1.5800400E-06	0.00E-00	2.3368505E-06
2.6000000E-03	1.9890400E-04	0.00E-00	1.8211882E-04
3.6000000E-03	9.6515400E-05	0.00E-00	8.5833585E-05
2.0000000E-03	2.8187800E-05	0.00E-00	2.3550387E-05
4.5000000E-03	1.2435600E-03	0.00E-00	1.2505876E-03
2.5000000E-03	7.5461100E-03	0.00E-00	7.5730099E-03
1.0000000E-02	3.4066600E-04	0.00E-00	3.0376393E-04
1.0000000E-02	4.5441200E-05	0.00E-00	3.9017552E-05
7.7000000E-01	2.8689100E-02	0.00E-00	2.8793103E-02
1.0000000E-01	1.4953700E-03	0.00E-00	1.4986067E-03

COMPARTMENT			Basic alphabet b_i	O_2 0.6529581	CO_2 0.281941	N_2 3.705233	H^+ 47.00022	OH^- 47.02972	CL^- 0.08005	Na^+ 0.08813	K^+ 0.04829	MISC PL 0.0155	MISC RC 0.0211275	$HB_4^{\pm}$ 0.0022725	CHARGE 0.0	$A^{\pm}$ 0.0	$B^{\pm}$ 0.0	C 0.0	D^- 0.0	Free-energy constants c_{ij}
1	X_{11}	O_2		1																	0.0
	X_{21}	CO_2			1																-7.69
	X_{31}	N_2				1															-11.52
	X_{41}	H_2O					1	1													-36.60
2	X_{12}	O_2		1																	-10.94
	X_{22}	CO_2			1																0.0
	X_{32}	N_2				1															0.0
	X_{42}	H^+					1								1						0.0
	X_{52}	OH^-						1							-1						0.0
	X_{62}	Cl^-							1						-1						0.0
	X_{72}	Na^+								1					1						0.0
	X_{82}	K^+									1				1						2.5966
	X_{92}	H_2O					1	1													-39.39
	$X_{10,2}$	HCO_3^-			1			1							-1						-21.35
	$X_{11,2}$	$H_2CO_3^-$			1		1	1													-32.84
	$X_{12,2}$	CO_3			1		-1	1							-2						6.26
	$X_{13,2}$	MISC PL										1			-1						0.0
3	X_{13}	O_2		1																	10.45
	X_{23}	CO_2			1																0.0
	X_{33}	N_2				1															-0.50
	X_{43}	H^+					1														0.0
	X_{53}	OH^-						1													0.0
	X_{63}	Cl^-							1												0.0
	X_{73}	Na^+								1											2.2435
	X_{83}	K^+									1										0.0
	X_{93}	H_2O					1	1													-39.39
	$X_{10,3}$	HCO_3			1			1													-21.49
	$X_{11,3}$	H_2CO_3			1		1	1													-32.84
	$X_{12,3}$	CO_3			1		-1	1													6.12
	$X_{13,3}$	MISC RC											1								0.0
	$X_{14,3}$	HB_4^-											1		-4						0.0
	$X_{15,3}$	HB_4O_2		1									1		-3	-1					-1.9028
	$X_{16,3}$	HB_4O_4		2									1		-2	-2					-2.8889
	$X_{17,3}$	HB_4O_6		3									1		-1	-3					-3.3622
	$X_{18,3}$	HB_4O_8		4									1			-4					-7.4854
4	X_{14}	$+H_2HB$					1									1					-15.639
	X_{24}	*HHB														1					0.0
	X_{34}	-HB					-1									1			-4		21 81
5	X_{15}	$*H_2HBO$					1										1				-16.79
	X_{25}	$*HHBO_2$															1				0.0
	X_{35}	$-HBO_2$					-1										1			-4	18.9779
6	X_{16}	HB^-																	1		0.0
	X_{26}	$-HCO_2$			1		-1												1		11.959
7	X_{17}	HBO_2																		1	0.0
	X_{27}	$-BOCO_2$			1		-1													1	12.899

Fig. 1—Data for Lung Level Respiration Model[2]

$A^{\pm}$ refers to an unoxygenated 1/4 hemoglobin molecule.
$B^{\pm}$ refers to an oxygenated 1/4 hemoglobin molecule.
C^- refers to an amphanion equivalent with respect to CO_2.
D^- refers to an oxyheme amphanion equivalent with respect to CO_2.

the values of the free-energy function at those minima yield essentially the same minimum. Neither solution satisfies the constraints exactly. The point to be made is that SUMT requires no delicate analysis to obtain an initial starting vector. Also note again that SUMT in conjunction with the rank annihilation of matrix inversion is extremely efficient in solving moderate-sized nonlinear programming problems.

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13. ABSTRACT

The equilibrium composition of homogeneous chemical reactions is a very important problem in studies of complex systems that arise in the study of certain physiological systems, rocket propulsion, reentry problems, etc. The aim of this report is to show that the sequential unconstrained minimization technique (SUMT) as exploited by Fiacco and McCormick is capable of solving this problem and indeed offers distinct advantages over the heretofore best available computational techniques. The power of this method for solving moderate-sized problems is illustrated by the choice of a 45-variable problem with 16 linear equality constraints.

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